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(54) Composition and Method for Stabilizing Beverages
Against Haze Formation

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This invention relates to the treatment of beverages with silica gel and polyvinylpyrrolidone to absorb high molecular weight proteins and polyphenols and stabilize the beverages against haze formation on storage or chilling.

5 Beverages such as beer, ale, wine, whiskey, and other products of the fermentation of cereals, fruits, and vegetables contain suspended or dissolved proteins, polyphenols such as tannins, and protein-tannin complexes. 10 These substances can form an insoluble precipitate on storage or chilling of the beverage and cause it to become hazy.

Compositions containing finely divided silicas and polyvinylpyrrolidone have been used to stabilize beverages 15 against haze formation. The silica adsorbs high molecular weight proteins and protein-tannin complexes and the polyvinylpyrrolidone absorbs polyphenols. The treated beverage is filtered or centrifuged to remove the adsorbent and haze-forming substances.

20 U. S. Patent 3,117,004 of McFarlane et al. discloses the use of a water insoluble polyvinylpyrrolidone, polyvinylpolypyrrolidone, to remove tannins from beer. The polyvinylpolypyrrolidone can be employed as an active coating on an inert carrier such as silica gel. In 25 U. S. Patent 3,554,759 of Beschke et al., beer is stabilized against clouding by treatment with a modified finely divided silica obtained by precipitating silica from an aqueous alkali metal silicate solution with an acid in the presence of water soluble polyvinylpyrrolidone or its

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water soluble derivatives. U. S. Patent 3,818,111 of Hoover discloses the separate addition in any order to beer of water soluble or colloiddally dispersible polyvinylpyrrolidone and polysilicic acid hydrosol or hydrogel. In Example 3 at columns 9 through 12, the stabilization provided by addition of a mixture is compared to that provided by separate addition of these components. German Patent Publication 19 07 610 of Suhner discloses an agent for stabilizing and clarifying beverages, especially beer. The agent is prepared by drying a hydrated freshly precipitated silicic acid to a powder with a particle size of 10 to 100 microns and a pH of 5.5 to 7.5 and mixing the fine particles with polyvinylpyrrolidone and/or other stabilizers.

The present invention provides a composition and method for stabilizing a beverage against haze formation. The composition comprises a mixture of a major amount of a silica gel and a minor amount of a water insoluble polyvinylpyrrolidone. The mixture is prepared by forming the gel in the presence of the polyvinylpyrrolidone and other fermented beverages. In accordance with the method, a beverage is contacted with a stabilizing amount of the composition. The composition substantially reduces the polyphenol concentration and haze formation on storage and chilling at low polyvinylpyrrolidone levels when used to treat high solids beer.

A water insoluble vinylpyrrolidone polymer such as polyvinylpolypyrrolidone, or co-polymer is used in the present invention. Suitable co-polymers include co-polymers of N-vinylpyrrolidone with vinyl esters such as vinyl formate, vinyl acetate, and vinyl chloride and with other vinyl

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monomers such as N-vinyl-3-methyl-2-pyrrolidone, N-vinyl-2-piperidone, N-vinyl-2-caprolactam, N-vinylsuccinimide, N-vinyl-3-morpholinone, N-vinyl-5-methyl-2-oxazolidinone, N-vinyl-5-ethyl-2-oxazolidinone, N-vinyl-2-oxazolidinone, and acrylamide. Suitable crosslinked water insoluble polymers of N-vinyl- α -pyrrolidone may be prepared in accordance with U. S. Patents 2,938,017 and 3,277,066 by polymerizing N-vinyl pyrrolidone in the presence of an alkaline catalyst.

The polyvinylpyrrolidone is a finely divided solid powder that has a weight median particle diameter of at least about 1 micron and preferably of about 5 to 20 microns. Water insoluble crosslinked polymers having a molecular weight of from about 300,000 to about 400,000 are especially preferred. A suitable water insoluble polyvinylpyrrolidone is sold under the trademark Polyclar AT by GAF Corporation. Polyclar AT clarifier is a high molecular weight, crosslinked polyvinylpyrrolidone powder that is insoluble in water, organic solvents, and strong mineral acids and alkali.

The silica used in the present invention is a silica gel and not a precipitated silica. A silica gel differs from a precipitated silica in that a gel has a network structure which encloses the whole liquid phase in which it is formed and a precipitated silica encloses only part of the liquid in which it is formed and settles out of the liquid as finely divided aggregates. See, Iler, The Colloid Chemistry of Silica and Silicates, pp. 128-160 (Ithaca, N.Y. 1955). A silica hydrogel is preferred because its

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high surface area and large pores provide superior adsorption.

The composition of the present invention generally has a weight median particle diameter of at least about 1 micron and preferably of from about 10 to about 100 microns.

- 5 Preferably, the composition has a water content of from about 20 to about 80 weight percent, especially of from about 40 to about 60 weight percent, and a pH of from about 1 to about 10, especially of from about 4 to about 6. The water content is measured as percent loss in weight
- 10 after heating at 950°C. for one hour minus the weight percentage of polyvinylpyrrolidone present in the composition and the pH is determined as that of a 5 weight percent aqueous slurry of the composition. The surface area of the composition is generally at least about 200 square meters
- 15 per gram and preferably is from about 400 to about 800 square meters per gram. The pore volume of the composition is generally from about 0.1 to about 1.0 cubic centimeters per gram and preferably is from about 0.1 to about 0.6 cubic centimeters per gram. The composition generally
- 20 has an average pore diameter of from about 15 to about 200 angstroms and preferably of from about 20 to about 60 angstroms. The surface areas and pore volumes were determined after drying for 3 hours at 750°F. (399°C.) by the nitrogen adsorption method described in Brunauer,
- 25 Emmett, and Teller, 60 J. Am. Chem. Soc. 309 (1938). The method was run to a P/P_0 of 0.967 so that pore diameters of from 14 to 600 angstroms were measured. The average pore diameter was calculated from the pore volume

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and surface area in accordance with the following equation

$$\text{average pore diameter} = \frac{4 \times \text{pore volume} \times 10^4}{\text{surface area}}$$

5 The silica gel is formed in the presence of the water insoluble, finely divided polyvinylpyrrolidone powder. Silica gel is typically prepared by mixing an aqueous alkali metal silicate solution, usually sodium silicate,
10 and an aqueous mineral acid solution, usually sulfuric acid, to form a silica hydrosol and allowing the hydrosol to set to a hydrogel. The composition of this invention may be prepared by adding the polyvinylpyrrolidone powder to the acid, silicate, or hydrosol and blending the mixture to
15 disperse the polymer and form a homogeneous mixture. Introduction of the polymer prior to gelation provides a uniform distribution of the polyvinylpyrrolidone throughout the silica hydrogel matrix.

The concentration of the acid solution is generally
20 from about 5 to about 70 percent by weight and the aqueous silicate solution commonly has a SiO_2 content of about 6 to about 25 weight percent and a weight ratio of SiO_2 to Na_2O of from about 1:1 to about 3.4:1. The reaction is generally carried out at a temperature of from about 60°F.
25 to about 175°F. (15-80°C.) and typically is carried out at ambient temperatures. The relative proportions and concentrations of the reactants are selected so that the hydrosol contains from about 5 to about 20 weight percent SiO_2 and has a pH of from about 1 to about 11 and typically of from

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about 1 to about 5. The hydrosol sets to a hybrid hydrogel mass containing silica, the polymer, and water in generally about 1 to about 90 minutes. The mass shrinks as it ages and undergoes syneresis and is
5 broken or cut up mechanically into granules.

The hydrogel granules are then washed with water or acidified water to remove residual alkali metal salts which are formed in the reaction. Acidified water, usually at a pH of from about 1.0 to about 5.0, preferably of from about
10 2.5 to about 4.5 is preferred. The acid may be a mineral acid such as sulfuric acid, hydrochloric acid, nitric acid, or phosphoric acid or a weaker acid such as formic acid, acetic acid, oxalic acid, citric acid, tartaric acid, nitriloacetic acid, ethylene diamine-tetraacetic acid, or
15 propionic acid. The water usually has a temperature of from about 40° to about 200°F. (4-94°C.). Alternatively, the hydrogel granules may be washed with a base which is usually ammonium hydroxide or a substituted ammonia, such as a water-soluble amine. Generally, the ammonium hydroxide
20 has a pH of about 8 to about 10 and a temperature of about 100 to about 200°F. (37-94°C.). The hydrogel is typically washed for a period of from about 6 to about 40 hours.

The washed hybrid hydrogel generally has a particle size ranging from about 1 micron to about 50 millimeters. The
25 hybrid is dried to the desired water content by conventional methods. Oven drying, rotary, drying, cascade drying,

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or any other known drying method may be employed. The composition may be dried and then ground to the desired particle size in a hammer mill or fluid energy mill or simultaneously dried and ground in such a mill using
5 heated air or steam as the grinding fluid.

The silica gel and polyvinylpyrrolidone contents of the composition may vary widely depending on the nature of the beverage that is treated. Generally, the polyvinylpyrrolidone is present in a minor amount that may range from
10 about 5 to about 25 weight percent of the composition. The silica gel (including the water present) comprises a major amount and preferably comprises from about 75 to about 95 weight percent of the composition.

The composition may be added to the beverage in the
15 form of a powder or mixed with sufficient water to form a paste or slurry prior to treatment of the beverage. A slurry is preferred to provide maximum contact of the beverage with the composition.

The amount of the composition that is effective for
20 stabilizing the beverage depends upon the nature of the beverage, the stage of its manufacture at which treatment is conducted, and the desired degree of clarity and chill haze stability. Generally, the composition is employed in an amount of from about 5 to about 25 pounds per 100 U. S.
25 barrels (20-100 grams per hectoliter) of the fermented beverage.

The treated beverage is aged for a period sufficient for the composition to adsorb haze-causing substances and settle out. The necessary aging time depends on the

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amount of the composition added and the initial and desired final turbidity and the type of beverage. In general, a contact time of from about 18 to about 32 hours is sufficient at typical loadings. After aging, 5 the coagulated substances are removed from the beverage, for example, by filtration, centrifugation, or decantation.

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The following examples further illustrate the composition and method of the present invention. The polyvinylpyrrolidone powder used in the Examples was Polyclar^(R) AT stabilizer of GAF Corporation which is a high molecular weight, cross-linked, water insoluble polyvinylpyrrolidone having a weight median particle diameter of about 10 microns. All percentages in the Examples are by weight.

Examples 1-9

- 10 A 36° Baume aqueous sulfuric acid solution having a temperature of 120°F. (49°C.) and a 36.5° Baume aqueous sodium silicate solution having a temperature of 100°F. (38°C.) were pumped into a mixing nozzle at flow rates of 68 liters per minute and 201 liters per minute
15 respectively. The resulting silica hydrosol had an SiO₂ content of 18 percent and a pH of 1.5.

- Portions of water insoluble polyvinylpyrrolidone powder were mixed for 30 seconds in a blender with two liter portions of the 18 percent
20 silica hydrosol. A high speed mixing setting was employed in Example 9 and a low speed setting in the remaining examples. The hydrosol and polyvinylpyrrolidone mixtures set to hydrogels in about 3 minutes. The hydrogels were washed for 24 hours with an aqueous
25 ammonia solution having a pH of 9.5 and a temperature of 185°F. (85°C.) in Examples 1-3 and a pH of 9.0 and a temperature of 180°F. (82°C.) in Example 7 and for 24 hours with an aqueous sulfuric acid solution having a pH of 3.5 and a temperature of 170°F. (77°C.) in

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Examples 4-5 and a pH of 3.0 and a temperature of 160°F. (71°C.) in Examples 8 and 9. The washed hydrogels were then partially dried and ground in an air classifying, rotary hammer mill at a classifier speed of 3000 to 3050
5 revolutions per minute and an inlet air temperature of 198 to 205°F. (92-96°C.). All of the milled product passed through a 325 mesh U. S. Standard Sieve. In Example 6, a portion of the product of Example 2 was further dried to a total volatiles content of 31.9
10 percent. The total volatiles content is the percentage loss in weight after one hour at 1750°F. (955°C.). The amounts of polyvinylpolypyrrolidone added to the hydrosol and the properties of the products are shown in Table I.

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Table I

Example No.	1	2	3	4	5
pH	7.78	8.93	9.32	4.91	4.19
Weight Median Particle Diameter (microns)	10.5	11.1	13.2	11.9	11.8
Polyvinylpyrrolidone (grams)	75	75	150	37.5	75
Total Volatiles (%)	52.8	51.2	36.94	58.1	52.7
Surface Area (m^2/g)	367	382	235	667	657
Nitrogen Pore Volume (cm^3/g)	0.88	0.83	0.84	0.58	0.38
Average Pore Diameter (angstroms)	96	87	143	35	23

After Drying for 3 hours at 750°F. (399°C.)

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Table I (continued)

Example No.	6	7	8	9
pH				
Weight Median Particle Diameter (microns)	8.93	8.94	4.66	4.63
Polyvinylpyrrolidone (grams)	11.1	17.4	16.6	14.3
	75	194	194	389
Total Volatiles (%)	31.9	40.7	79.0	75.7
After Drying for 3 hours at 750°F. (399°C.)				
Surface Area (m^2/g)	382 ¹	279	523.0	451.0
Nitrogen Pore Volume (cm^3/g)	0.83	0.81	0.25	0.25
Average Pore Diameter (angstroms)	87	116	19	22

1. This measurement was made on the product of Example 2.

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Certain of these products were used to treat beers obtained after krausening in a commercial brewery. The krausened beer was chilled overnight at 30°F. (-1.1°C.) and placed in one gallon containers. Aqueous slurries containing

- 5 10 weight percent of the products were respectively added to one gallon portions of beer at the loadings shown in Table II and one-third of a gallon of carbonated water was added to the beer. The beer was then chilled overnight at 30°F. (-1.1°C.) and under 17 to 20 pounds
- 10 per square inch of carbon dioxide pressure. A diatomaceous earth filter aid was added to the chilled beer at a loading of 0.4 lbs. per barrel as a slurry in 50 milliliters of carbonated water. The beer was then
- 15 filtered through a Walton DE filter frame using a precoat of 5.04 grams of the filter aid and 0.27 gram of cellulose fiber. Filtration was conducted over a period of 30 to 40 minutes and a maximum pressure of 30 to 40 pounds per square inch was reached in the system. Immediately after
- 20 filtration, the beer was hand bottled under a carbon dioxide pressure of 17 to 20 pounds per square inch. Three haze measurements were made on separate bottles of the beer after chilling at 30°F. (-1.1°C.) for 3 days, after
- 25 aging at 100°F. (37.8°C.) for one week and chilling at 30°F. (-1.1°C.) for 3 days, and after aging at 100°F. (37.8°C.) for two weeks and chilling at 30°F. (-1.1°C.) for 3 days. The haze readings were measured by visual comparison with standard beers of known turbidity values of 0.5, 2.0, 4.0, 10, and 15 and are shown in Table II.

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Table II

Example	Loading (g. per gal./ lbs. per 100 bbls.)	Haze Values		
		3 Day Chill	1 Week Age and 3 Day Chill	2 Weeks Age and 3 Day Chill
1	4.16/32.1	1.0	5.5	12.0
1	4.76/36.7	0.7	3.5	7.5
2	2.43/18.7	1.0	6.0	11.0
2	3.04/23.4	0.5	4.0	5.0
2	3.64/28.1	0.5	5.0	8.5
3	1.59/12.3	1.0	1.0	1.0
3	1.79/13.8	0.5	1.0	1.0
3	1.35/10.4	1.0	12.0	10.0
3	1.79/13.8	0.5	3.0	6.0
6	2.21/17.0	0.5	1.5	8.0
6	3.30/25.4	0.5	1.0	6.0
6	2.7/20.8	0.5	4.0	4.0
6	3.6/27.8	0.5	2.0	2.0
6	4.5/34.7	0.5	1.0	1.0

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Table II (continued)

Example	Loading (g. per gal./ lbs. per 100 bbls.)	Haze Values		
		3 Day Chill	1 Week Age and 3 Day Chill	2 Weeks Age and 3 Day Chill
7	1.5/11.6	1.0	15.0	>15.0
7	1.8/13.9	1.0	13.0	>15.0
7	2.1/16.2	1.0	8.0	13.0
7	2.4/18.5	0.5	2.0	4.0
8	1.88/14.5	0.5	1.0	1.0
9	1.56/12.0	0.5	0.5	0.5
Comparative Polyvinylpoly- pyrrolidone alone	0.45/3.47	0.5	15.0	>15.0

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The polyphenol levels after treatment with certain of the products of Table I were determined by the European Brewery Convention Method for Polyphenol Determination in Beer and are shown in Table III. The Convention
5 Method is described in Gress et al., "Polyphenols in Beer", J.Am.Soc.Brew.Chem., Vol. 35(3), pp. 131-132 (1977).

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Table III

Example	Loading (g. per gal./ lbs. per 100 bbls.)	Polyphenol Levels (p.p.m.)		
		Initial	Treated	Removal
3	1.35/10.4	130	130	0
3	1.79/13.8	130	100	23
6	2.7/20.8	130	101	22
6	3.6/27.8	130	95	27
6	4.5/34.7	130	96	26
7	2.1/16.2	130	98	25
7	2.4/18.5	130	94	28
Comparative Polyvinylpoly- pyrrolidone alone	0.45/3.47	199	148	26

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The results demonstrate that the compositions of the present invention provide excellent chillproofing and polyphenol reductions at low polyvinylpyrrolidone loadings.

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WHAT IS CLAIMED IS:

1. A composition for stabilizing beverages against haze formation comprising a mixture of a major amount of a silica gel and a minor amount of a water insoluble polyvinylpyrrolidone, said mixture prepared by forming the gel in the presence of the polyvinylpyrrolidone.
2. The composition of claim 1 in which the gel is a hydrogel and the composition has a water content of from about 20 to about 80 weight percent.
3. The composition of claim 1 in which the gel is formed in the presence of polyvinylpyrrolidone having a weight median particle diameter of at least about 1 micron.
4. The composition of claim 2 in which the gel is formed in the presence of polyvinylpyrrolidone having a weight median particle diameter of at least about 1 micron.
5. The composition of claims 3 or 4 in which the mixture is prepared by dispersing the polyvinylpyrrolidone in a silica hydrosol, gelling the hydrosol, and grinding the mixture.
6. The composition of claim 1 in which the gel is formed in the presence of polyvinylpyrrolidone having a weight median particle diameter of from about 5 to about 20 microns.
7. The composition of claim 2 in which the gel is formed in the presence of polyvinylpyrrolidone having a weight median particle diameter of from about 5 to about 20 microns.
8. The composition of claims 6 or 7 in which the mixture is prepared by dispersing the polyvinylpyrrolidone in a silica hydrosol, gelling the hydrosol, and grinding the mixture.
9. The composition of claim 1 or 2 in which the gel is formed at a pH of from about 1 to about 5 and the mixture is washed with an acidic aqueous solution to provide a composition having a pH of from about 4 to about 6.
10. The composition of claim 1 wherein the gel undergoes syneresis and the polyvinylpyrrolidone is uniformly distributed throughout the gel.

11. A method for stabilizing a beverage against haze formation comprising contacting the beverage with a stabilizing amount of a composition comprising a mixture of a major amount of a silica gel and a minor amount of a water insoluble polyvinylpyrrolidone, said mixture prepared by forming the gel in the presence of the polyvinylpolypyrrolidone.

12. The method of claim 11 in which the gel is a hydrogel and the composition has a water content of from about 20 to about 80 weight percent.

13. The method of claim 11 in which the gel is formed in the presence of polyvinylpolypyrrolidone having a weight median particle diameter of at least about 1 micron.

14. The method of claim 12 in which the gel is formed in the presence of polyvinylpolypyrrolidone having a weight median particle diameter of at least about 1 micron.

15. The method of claims 13 or 14 in which the mixture is prepared by the polyvinylpolypyrrolidone in a silica hydrosol, gelling the hydrosol, and grinding the mixture.

16. The method of claim 11 in which the gel is formed in the presence of polyvinylpolypyrrolidone having a weight median particle diameter of from about 5 to about 20 microns.

17. The method of claim 12 in which the gel is formed in the presence of polyvinylpolypyrrolidone having a weight median particle diameter of from about 5 to about 20 microns.

18. The method of claims 16 or 17 in which the mixture is prepared by dispersing the polyvinylpolypyrrolidone in a silica hydrosol, gelling the hydrosol, and grinding the mixture.

19. The method of claim 11 in which the gel is formed at a pH of from about 1 to about 5 and the mixture is washed with an acidic aqueous solution to provide a composition having a pH of from about 4 to about 6.

20. The method of claim 11 wherein the gel undergoes syneresis and the polyvinylpolypyrrolidone is uniformly distributed throughout the gel.

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21. A method of stabilizing beer against haze formation comprising contacting the beer with a stabilizing amount of a composition comprising a mixture of a major amount of a silica hydrogel and a minor amount of a water insoluble polyvinylpyrrolidone, said mixture prepared by dispersing a water insoluble polyvinylpyrrolidone powder having a weight median particle diameter of about 10 microns in a silica hydrosol, gelling the polyvinylpyrrolidone-containing hydrosol, and drying and grinding the hydrogel to a water content of from about 40 to about 60 weight percent and a weight median particle diameter of from about 10 to about 100 microns.

22. A method of stabilizing beer against haze formation comprising contacting the beer with a stabilizing amount of a composition comprising a homogeneous mixture of a major amount of a silica hydrogel and a minor amount of a water insoluble polyvinylpyrrolidone, said mixture prepared by dispersing a water insoluble polyvinylpyrrolidone powder having a weight median particle diameter of about 10 microns in a silica hydrosol, gelling the polyvinylpyrrolidone-containing hydrosol so that the hydrogel undergoes syneresis and the polyvinylpyrrolidone is uniformly distributed throughout the hydrogel, and drying and grinding the hydrogel to a water content of from about 40 to about 60 weight percent and a weight median particle diameter of from about 10 to about 100 microns.

